AD-A202 307

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-81-C-0776

TASK No. NR 051-775

TECHNICAL REPORT #34

GEOMETRICAL STRUCTURE OF ADLAYERS ON IMMERSED ELECTRODES

by

Joseph G. Gordon II*, Owen R. Melroy* and Lesser Blum**

IBM Research Division
Almaden Research Center
650 Harry Road
San José, California 95120-609

*Department of Physics, POB AT, Faculty of Natural Sciences,
**University of Puerto Rico, Río Piedras, Puerto Rico 00931

8 8 12 14 ^ ⁻ ¹

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #34	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Geometrical Structure of Adlayers on Immersed Electrodes		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Joseph G. Gordon II, Owen R. Melroy and Lesser Blum		8. CONTRACT OR GRANT NUMBER(s) N00014-81-C-0776
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics University of Puerto Rico Box AT, Río Piedras, P.R. 00931		10. PROGRAM ELEMENT. PROJECT. TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Code 472 Office of Naval Research Arlington, VA 22217		12. REPORT DATE 11-4-88
		13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in Springer series on surface physics.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) X rays, electrode, interface, exafs, structure		

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Lead and copper monolayers (produced by underpotential deposition) on silver (III) and gold(III) surfaces, respectively, have been characterized by x-ray absorption spectroscopy and x-ray diffraction. The experiments were performed in situ, with the electrode immersed in aqueous electrolyte, and at a controlled potential. A combination of grazing incidence excitation and fluorescence detection (for x-ray absorption) provided the required sensitivity and surface selectivity. The metal adlayers are fully reduced (zero valent). Lead forms

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

a well ordered two dimensional solid with a close packed hexagonal structure. Its lattice is slightly compressed relative to bulk lead and is incommensurate with the underlying silver lattice. The copper EXAFS is consistent with a commensurate overlayer with the copper atoms in the three fold sites. Oxygen atoms of the first layer of water or adsorbed electrolyte lie at a well defined distance from the metal adlayers.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Geometrical Structure of Adlayers on Immersed Electrodes.

Joseph G. Gordon II
Owen R. Melroy
IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

Lesser Blum
Physics Department,
University of Puerto Rico
Rio Piedras, PR 00931.

ABSTRACT

Lead and copper monolayers (produced by underpotential deposition) on silver(111) and gold(111) surfaces, respectively, have been characterized by x-ray absorption spectroscopy and x-ray diffraction. The experiments were performed *in situ*, with the electrode immersed in aqueous electrolyte, and at a controlled potential. A combination of grazing incidence excitation and fluorescence detection (for x-ray absorption) provided the required sensitivity and surface selectivity. The metal adlayers are fully reduced (zero valent). Lead forms a well ordered two dimensional solid with a close packed hexagonal structure. Its lattice is slightly compressed relative to bulk lead and is incommensurate with the underlying silver lattice. The copper EXAFS is consistent with a commensurate overlayer with the copper atoms in the three fold sites. Oxygen atoms of the first layer of water or adsorbed electrolyte lie at a well defined distance from the metal adlayers.

1. INTRODUCTION

In discussions of dynamics one assumes, explicitly or implicitly, a specific underlying geometric structure. For the solid:vacuum interface, this structural picture is based on the results of fairly direct experiments, eg. RHEED, LEED, electron microscopy, or STM. For the metal:electrolyte interface, what is known is inferred from thermodynamic, kinetic, and optical measurements coupled with theoretical treatments based on highly idealized models which accurately describe only the diffuse double layer, or space charge region, within 10-100 Å of the electrode surface. While these measurements are sensitive to structure, and provide a reasonable picture of the interface, they cannot directly reveal structure at the atomic or molecular level.

In recent years there have been considerable advances in the development of new, primarily spectroscopic, probes of the solid:liquid interface.[1-9] These provide information about the identity and quantity of interfacial species and possibly their orientation, but do not directly reveal the geometrical arrangement of molecules at the interface. Another approach has been to apply ultrahigh vacuum (UHV) surface spectroscopic techniques.[10, 11] As these rely primarily on particles as probes, they are not effective in solution because the propagation distances are too short. For application, they require transfer of the electrode from the electrolytic medium into vacuum and therefore present the serious question of whether the examined surface is really identical to the surface in solution. Transfer from normal pressure (24 torr, the vapor pressure of water at 25°C) to 10^{-10} torr represents a destabilization (ΔG) by approximately 16 Kcal/mol for any surface structure stabilized by water. Since the solvent (water) is not a contaminant, but rather an essential component of the interface, one really needs to observe the structure *in situ* to have confidence in the results.

X-rays are the most promising probes to do this. X-rays with energies exceeding about 6 KeV do penetrate water and have wavelengths comparable to atomic spacings, so they can provide direct geometrical information. This article reports the use of *in situ* surface extended X-ray absorption fine structure (SEXAFS) and grazing incidence x-ray scattering (GIXS) to study metal adlayers under normal electrochemical conditions, i.e., under liquid electrolyte and at controlled potential. Two systems will be discussed, copper on Au(111) and lead on Ag(111).

Both of the above combinations exhibit underpotential deposition (UPD).[12] That is, the first layer of metal is deposited at potentials less negative than the formal thermodynamic deposition potential. In this initial deposition, the coverage changes from zero to saturation over a very narrow range and then remains constant until the potential for bulk deposition is reached. The experiments described below were performed at potentials in this region of constant coverage.

2. EXPERIMENTAL

As surface probes, X-rays have three major problems:

1. The scattering and absorption cross sections are small. For example, absorption by a monolayer of lead just above the L_{III} edge would result in a change in transmittance of $\Delta T/T = 5 \times 10^{-5}$.

2. They are not inherently surface selective, a consequence of their weak interaction with matter.

3. Scattering by "uninteresting" matter (which is present in much greater quantity than the interesting stuff) generates a large background signal.

We have used a combination of techniques to overcome these problems (See Fig. 1):

1. The exciting x-rays strike the sample at a grazing angle so that they are totally externally reflected. (At x-ray wavelengths, the refractive index of matter is less than one.) This restricts the penetration of the x-rays (the evanescent wave) to less than 50 Å.

2. The surface layer differs in elemental composition from the substrate (hence, its fluorescence line is at a different energy).

3. The x-ray flux is very high (synchrotron source).

4. The overlayers, electrolyte and window, are thin (< 50 μm), minimizing scatter.

5. For SEXAFS, the x-ray absorption is measured by detecting the characteristic fluorescence emitted by the excited atoms rather than by measuring a change in transmittance.

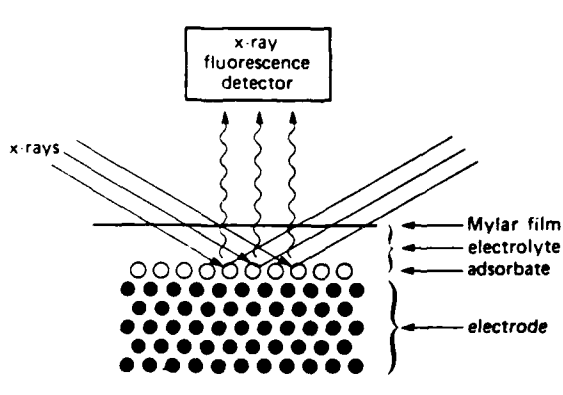6. For GIXS, the incident beam is highly collimated, 1 mrad (synchrotron source).

Figure 1. Schematic of the *in situ* x-ray absorption experiment. The angle of incidence is exaggerated. The scattering experiment is similar, except that the detector is moved.

Au(111) or Ag(111) electrodes were epitaxially grown by evaporation in vacuum onto a mica substrate held at elevated temperature.[13] This electrode formed one side of a thin layer cell. The other side was a 6.35 μm thick mylar sheet. When the electrode assembly was lowered into the electrolyte reservoir, the mylar film floated on the surface exposing the metal film to the bulk solution. The metal adlayers were deposited in this position. After deposition, electrolyte was withdrawn until just the bottom of the electrode was immersed. A thin layer of solution (estimated to be less than 50 μm thick) was held between the mylar film and the electrode surface by capillary action. In this way, the thin layer remained in electrical (and physical) contact with the electrolyte reservoir in which were situated the counter (Pt) and reference (Ag/AgCl, 3 M KCl)

electrodes. Diffusion from the reservoir into the thin solution layer was very slow and even permitted polarization of the electrode negative of the formal deposition potential without significant additional metal deposition. The copper monolayer was deposited at +0.13 V from 5 x 10⁻⁵ M CuSO₄ in 0.5 M sulfuric acid solution. The lead monolayer was deposited at -0.53 V from 5 x 10⁻⁵ M lead acetate in a solution of 0.5 M sodium acetate and 0.1 M acetic acid.

For both the SEXAFS and GIXS experiments, the x-ray beam was incident through the mylar cover sheet at a grazing angle (< 0.5°). For EXAFS, the characteristic fluorescence lines were isolated by absorption filters (Ni for Cu and Ge for Pb) and an energy dispersive solid state detector (high purity Ge). The EXAFS data were analyzed in the standard way with interatomic distances being obtained by fitting the oscillatory part of the EXAFS equation to the experimental fine structure with phase shifts derived experimentally from model compounds.[14] Details of the cells and apparatus for both types of measurement are published elsewhere.[15, 16, 17]

3. RESULTS

3a. Cu on Au(111)

For these experiments, the gold electrode was poised at at +0.13 V in the region of saturated UPD coverage. From electrochemical and other measurements, the coverage at this potential is approximately one copper atom per surface gold atom and there is strongly suggestive evidence that the the copper layer is ordered and commensurate. To date, however, this has not been directly verified.[12, 18] The x-ray absorption spectrum of the copper adlayer was measured at the copper K-edge and is shown in Fig. 2. That this spectrum originates from reduced copper on the electrode surface was demonstrated by changing the potential to +0.5 V, where the UPD layer is oxidized to Cu²⁺, and recording another spectrum. (The copper ions are trapped by the thin layer cell and, hence, remain in the x-ray beam.) Before (solid) and after (dashed) spectra are shown in the inset in Fig. 2. The spectrum of the oxidized material (dashed curve) differs significantly from that of the UPD layer. First, the absorption edge is shifted about 4 eV to higher energy, consistent with the increase in oxidation state, and suggesting that the UPD layer is fully reduced. Second, there is a strong resonance peak just above the edge which is absent in the spectrum of the UPD layer. This 'white line' is characteristic of Cu(II). Indeed the dashed spectrum is identical with that from an authentic copper sulfate solution.
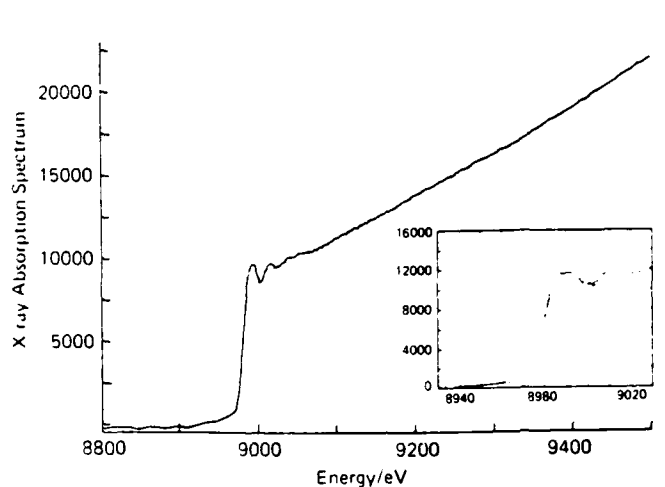
Figure 2. X-ray absorption spectrum at the Cu K$_\alpha$ edge for Cu on Au(111); electrode potential 0.13 V. Insert: Edge region at 0.13 V (dashed) and 0.50 V (solid).

The fine structure extracted from the absorption spectrum (Fig. 2) is shown in Fig. 3 along with the radial structure function (RSF) obtained by Fourier

transformation. The dashed line in Fig. 3 is the filtered fine structure obtained by inverse transformation of the RSF between 1 and 4 Å.
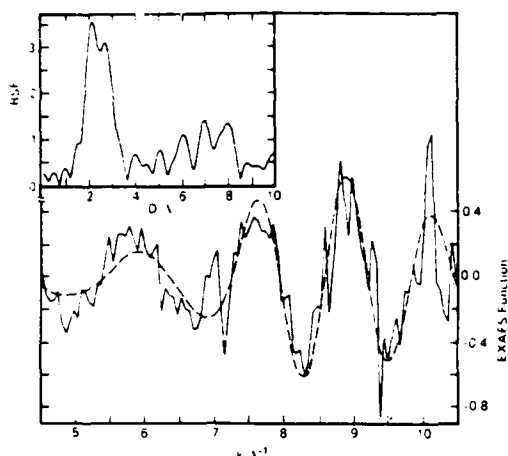

Figure 3. Solid line: EXAFS function for Cu on Au(111); Dashed line: Fourier filtered EXAFS (between 1 and 4 Å); Insert: Radial structure function (RSF) derived by Fourier transformation of EXAFS between k = 4 and 11 Å⁻¹.

Because the sample is a single crystal and the synchrotron x-ray beam is polarized, one can obtain information on orientation well as distance.[19] This is because the contribution of a given absorber-scatterer atom pair to the total EXAFS intensity is proportional to the square of the dot product of the x-ray beam electric field (polarization) vector and the atom-atom vector, or

$$N_{eff} = 3 \sum_{j=1}^{N} \cos^2 \theta_j,$$

where N_{eff} is the apparent number of atoms in the ith coordination shell, θ_j is the angle between the vectors and the summation is over all the atoms j in the ith coordination shell. Hence, atom pairs whose connecting vectors are parallel to the electric field vector (polarization direction) contribute significantly to the fine structure oscillations, whereas atom pairs whose connecting vectors are perpendicular to the polarization direction do not.

Accordingly, SEXAFS spectra were obtained in two different configurations: 1) with the x-ray beam polarized parallel [15] and 2) perpendicular [20] to the the plane of the electrode. The results are summarized in Table I. (The curves in Fig. 2 and 3 are for the parallel polarization.)

Table I. Interatomic distances for Cu on Au(111)

	$\updownarrow$	$\longleftrightarrow$
Cu-Cu	—	2.92±.03Å
Au-Cu	2.5±.06Å	2.58±.03Å
Cu-O	2.05±.03Å	—

The spectra for the parallel polarization yield two peaks in the RSF corresponding to copper-gold and copper-copper scattering. The copper-copper distance is identical within experimental error to the gold-gold distance (2.89 Å) in the (111) surface. Furthermore, copper-copper scattering is observed only for parallel polarization

indicating that all the copper atoms lie in the same plane. Copper-gold scattering is observed in both polarizations. This means that the copper atoms do not occupy atop sites. There is no evidence for more than one copper-gold distance, indicating that the copper atoms occupy a single symmetrical site. The amplitude of the copper-gold scattering is consistent with the three fold hollow as the adsorption site. Considered in combination with the coverage, these data indicate that the copper adlayer is commensurate with the gold lattice and that the copper atoms occupy three fold hollows.

Surprisingly, the RSF from the SEXAFS spectrum in perpendicular polarization has a second peak at a shorter distance than copper-gold. Judging from the shape of the amplitude function, it involves scattering from a light atom, presumably oxygen. If this assignment is correct, and since copper oxide is not stable in acid, this oxygen must be from interfacial water or adsorbed sulfate. Furthermore, this scattering is observed only in perpendicular polarization, so this atom sits directly above a copper atom. We believe that the most likely candidate is adsorbed sulfate, and therefore propose that the local site geometry about a copper atom in the UPD layer on gold(111) is as depicted in Fig. 4.
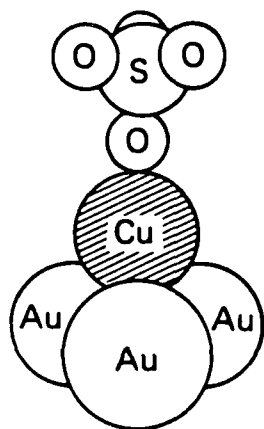

Figure 4. Local site geometry around copper.

3b. Pb on Ag(111)

The lead layer was studied by both SEXAFS [16] and surface diffraction [17, 21] at -0.53 V which is in the region between underpotential and bulk deposition. The coverage here, evaluated from the total charge transferred, is 1.6×10^{-9} mol/cm^2 (9.4×10^{14} atom cm$^{2)}$, close to that expected for a hexagonal close packed layer with bulk lead spacing. Reflectance [7] and ellipsometry [8] measurements support this interpretation, but there has been no direct structural determination. The X-ray absorption spectra were recorded at the Pb L_{III} edge with the x-ray beam polarized perpendicular to the electrode surface. As above, comparison of the spectra before and after oxidation of the adlayer demonstrated that the analyzed spectrum arose from a reduced lead layer on the silver surface. Analysis of the EXAFS reveals only one distance and it is too short to be Pb-Ag. Furthermore, the amplitude function is compatible only with scattering from a first row element. Given the composition of the solution, the most likely candidate is oxygen, from either water or acetate. With this assignment, a Pb-O distance of 2.33 ± 0.02 Å is obtained. This is longer than in PbO$_2$ (2.16-2.22 Å) or red PbO (2.30 Å) and is consistent with coordination to lead in a more reduced oxidation state.

An EXAFS spectrum was also obtained at an electrode potential of -1.0 V. Even though this is far negative of the reversible lead potential, the thinness of the cell limited diffusion so that there was no appreciable further deposition of lead during the data collection. The spectrum closely resembles that at -0.53 V. Analysis yields a single Pb-O distance of $2.38 \pm .02$ Å. No Pb-Ag scattering was detected. The Pb-O distance is

0.05 Å longer than at -0.53 V, and is consistent with repulsion of a charged or, at least, strongly dipolar adsorbate by a more negatively charged electrode.

The apparent absence of Pb-Ag scattering requires comment. It is probably the result of a large Debye-Waller factor for lead and the incommensurate nature of the adlayer. Large thermal motion is expected from lead's low melting point (600 K). Also, the melting point of Pb monolayers on Cu single crystals is reported to be even lower than the bulk value.[22] It is reasonable to expect Pb to exhibit similar behavior on Ag. Support for this view comes from the observation that the x-ray absorption spectrum of lead foil obtained during this study did not exhibit any fine structure. Furthermore, the Pb adlayer is certainly not commensurate with the underlying Ag lattice because of the large difference between the atomic radii of Pb and Ag (1.75 and 1.44 Å, respectively). The saturation coverage, given above, is consistent with a hexagonal close-packed monolayer with the normal Pb-Pb spacing. The effects of thermal motion and an incommensurate structure are similar and are not possible to distinguish from EXAFS data alone.

In this EXAFS experiment, the X-ray beam was polarized perpendicular to the electrode surface so information could not be obtained on the Pb-Pb spacing which would lie in the plane of the electrode and hence perpendicular to the E vector. This in-plane structure was probed by x-ray diffraction.[17]
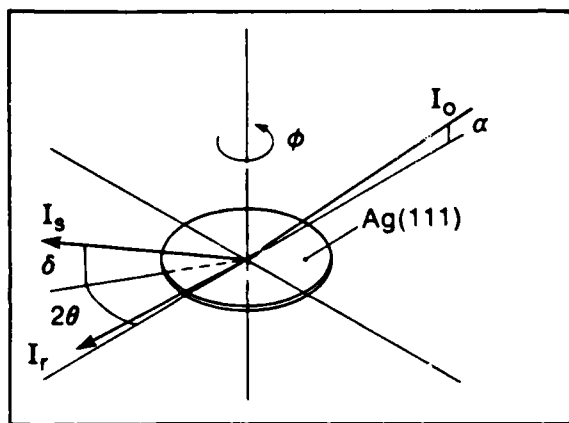

Figure 5. Scattering geometry: α is the incident angle, δ the output angle, θ the scattering angle, and ϕ the azimuthal angle of the sample.

Figure 5 illustrates the scattering geometry and defines the necessary angles. Figure 6 shows a radial (θ - 2θ) scan for the (10) reflection. This peak was confirmed to result from the lead monolayer by observing its disappearance when the electrode was poised at 0 V, at which potential, lead is oxidized to Pb^{2+} and dissolves in the solution. The relatively large background is due primarily to diffuse scattering from the thin layer of solution covering the electrode. Identical diffraction peaks are observed at 60° intervals, consistent with the six fold symmetry of a hexagonal layer. The (11) and (20) reflections were also observed, each with the expected six fold symmetry. The in-plane nearest neighbor distance, calculated from the diffraction angle, is 3.459 Å. This represents a 1.2% contraction from the distance in bulk lead (3.501 Å). From the full width half maximum (FWHM) of the peak, 0.037 Å⁻¹, the lead domains are estimated to be > 150 Å in diameter. This is comparable to that observed for a lead monolayer on copper (110) in UHV.[23]

Actually, there are two equivalent orientations of the lead adlayer on the silver surface as can be seen from Fig. 7, which shows an extended rocking (ϕ) scan of the (10) reflection. A straight line background has been subtracted from this data. The are two peaks rotated ±4.4°, respectively, from the Ag ($\bar{2}$11) direction, which is defined as ϕ = 0. A similar pair of peaks rotated ±4.4° from the corresponding silver direction is observed for each of the other reflections. The difference between the intensities of the + 4.4° and -4.4° are real. We do not know its origin, but presume that it is caused by
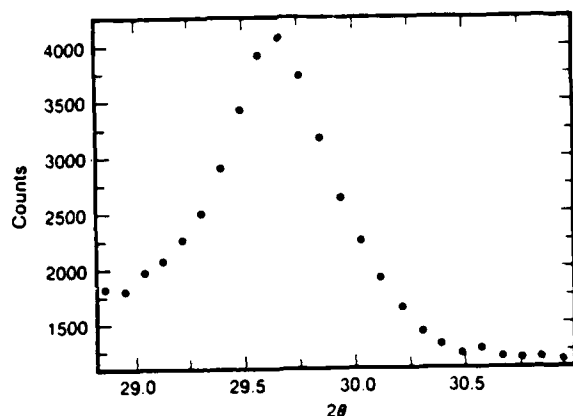
Figure 6. Radial scan at $\phi = 4.4°$ and $\alpha = \delta = 0.54°$

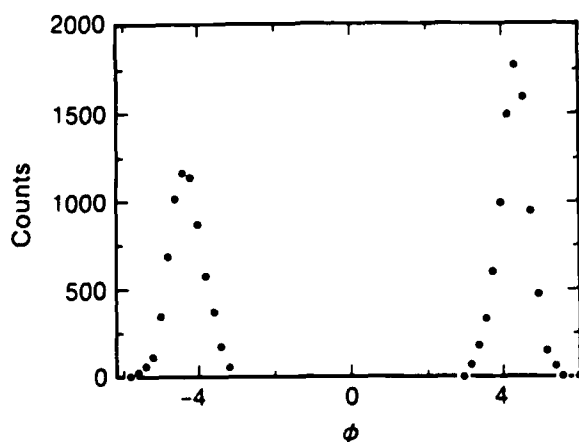**Figure 7.** Rocking scan of (10) reflection of Pb on Ag(111) at $2\theta = 29.688°$ and $\alpha = \delta = 0.54°$.

an anisotropic nucleation process. A similar difference was observed for O_2 and D_2 on graphite using LEED.[24]

Figure 8 illustrates the proposed structure of UPD lead on a silver (111) surface. The lead overlayer is ordered and epitaxial, but incommensurate with the silver lattice, and is rotated with respect to the silver lattice by 4.4°. This rotation angle is less than the 6.5° predicted by the McTague and Novaco model[25] but is in close agreement with that observed by Takayangi et al.[7] in their LEED study of vacuum deposited lead on silver (111).

4. DISCUSSION

SEXAFS and GIXS are complementary techniques, one probing local geometry and the other long range order. Together, they create a fairly detailed and unambiguous picture of the structure of UPD Pb on Ag(111). At full coverage, the Pb layer is hexagonally close packed, incommensurate with the substrate, and compressed 1.2% with respect to bulk metal. Acetate anions (probably) are adsorbed to the lead layer through oxygen atoms. X-ray scattering is not so easily applied to Cu on Au(111) since the adlayer diffraction peaks would coincide with those of the substrate and only small intensity differences would differentiate the bare from the adsorbate covered surface. Nevertheless, making use of the polarization dependence of the SEXAFS spectrum provides a quite detailed structural picture. An oxygen atom, probably from adsorbed
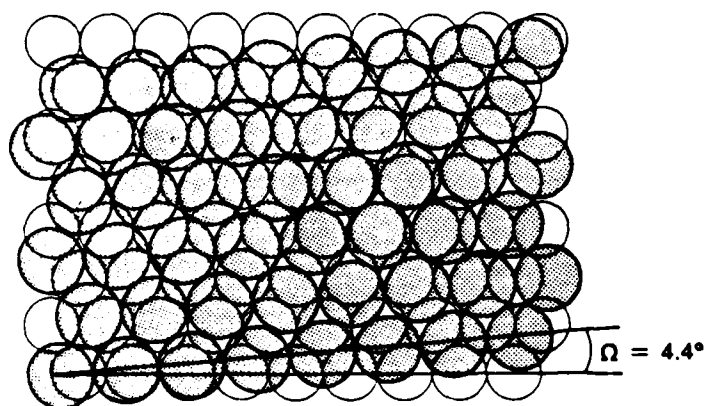
$\Omega = 4.4°$

Figure 8. Proposed structure of Pb monolayer. Open circles represent the substrate silver atoms and shaded circles the overlying lead atoms.

sulfate, sits directly atop the Cu atom. The Cu atoms occupy three-fold hollow sites and form a a (1 x 1) commensurate superlattice with the gold substrate. Although the SEXAFS cannot provide direct proof of long range order, it is hard to envisage another model which will fit all of the data, especially in light of the supporting evidence from the *ex situ* RHEED data of Nakai *et al.*[18]

These two examples demonstrate that x-ray techniques can yield unambiguous structural information from immersed surfaces and open up the realm of *in situ* investigation of interfaces of electrochemical interest. They also show that well-ordered surfaces do exist under solution, despite the high concentration of water molecules. Furthermore, at least in these two specific cases, the adlayers have structures very similar to those observed for the same pair of metals in vacuum.

References

1. Proc. Int. Conf. on Non-Traditional Approaches to the Study of the Solid Electrolyte Interface. Eds., T.E. Furtak, K.L. Kliewar, and D.W. Lynch, Surf. Sci., 101 (1980)

2. R. Chang and T. Furtak: Surface Enhanced Raman Scattering, (Plenum Press, New York, 1982)

3. M. Weaver, F. Barz, J. Gordon and M. Philpott: Surface Science, 125, 409 (1983)

4. K. Kinimatsu, H. Seki, W. Golden, J. Gordon and M. Philpott: Langmuir, 2, 464 (1986)

5. R. Corn, M. Romagnoli, M. Levenson and M. Philpott: J. Chem. Phys., 81, 4127 (1984)

6. G. Richmond: Langmuir, 2, 132 (1986)

7. K. Takayanagi, D. Kolb, K. Kambe and G. Lehmpfuhl: Surface Science, 100, 407 (1980)

8. R. Muller and J. Farmer: Surface Science, 135, 521 (1983)

9. J. Gordon and S. Ernst: Surface Science, 101, 499 (1980)

10. D. Kolb: In Advances in Electrochemistry, H. Gerischer and C. Tobias, Eds., Vol II, (Wiley, New York, 1978) p.125

11. A. Hubbard: Acc. Chem. Res., 13, 177 (1980)

12. D. Dickertmann, F. D. Koppitz and J. W. Schultze: Electrochim. Acta 21, 967 (1976)

13. K. Reichelt and H. O. Lutz: J. Cryst. Grow., 10, 103 (1971)

14. P. A. Lee, P. A. Citrin, P. Eisenberger, and B. M. Kincaid: Rev. Mod. Phys., 53, 769 (1981)

15. O. R. Melroy, M. G. Samant, G. L. Borges, J. G. Gordon II, L. Blum, J. H. White, M. J. Albarelli, M. McMillan and H. D. Abruna: Langmuir, in press

16. M. Samant, G. Borges, J. Gordon, L. Blum and O. Melroy: J. Am. Chem. Soc., 109, 5970 (1987)

17. M. Samant, M. Toney, G. Borges, L. Blum, and O. Melroy: Surf. Sci., 193, L29 (1988)

18. Y. Nakai, M. S. Zei, D. M. Kolb, and G. Lehmpfuhl: Ber. Bunsenges. Phys. Chem., 88, 340 (1984)

19. J. Stohr, R. Jaeger, S. Brennan: Surf. Sci., 117, 503 (1982)

20. L. Blum, H. Abruna, J. White, J. Gordon, G. Borges, M. Samant and O. Melroy: J. Chem. Phys., 85, 6732 (1986)

21. M. Samant, M. Toney, G. Borges, L. Blum, and O. Melroy: J. Phys. Chem., in press

22. J. Henrion and G. E. Rhead: Surf. Sci, 29, 20 (1972)

23. S. Brennan, P. H. Fuoss, and P. Eisenberger: Phys. Rev. B, 33, 3678 (1986)

24. M. Toney and S. Fain: Phys. Rev. B, 36, 1248 (1987); J. Chui and S.C. Fain: J. Vac. Sci. Techn., A5, 710 (1987)

25. J. P. McTague and A. D. Novaco: Phys. Rev. B, 19 (10), 5299 (1979)